Evaluating a solvent extraction process route incorporating nickel preloading of Cyanex 272 for the removal of cobalt and iron from nickel sulphate solutions

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ABSTRACT

Crude nickel sulphate solutions are produced during the first stage leach of Platinum Group Metal (PGM) containing converter matte in a Sherrit® atmospheric matte leach process. Iron and cobalt sulphates contaminate the nickel sulphate stream due to dissolution during the matte leach process. While iron is an unwanted contaminant, cobalt sulphate production presents a potentially valuable by-product, as long as removal of these metal ions does not introduce other forms of contamination into the solution.

Experimental work was performed to evaluate the removal of 1 g/l cobalt and 3 g/l iron from a sulphuric acid leach solution containing 80 g/l nickel using solvent extraction with Ni-Cyanex 272. The effects of various process parameters on preloading, extraction, and stripping were investigated. Based on full factorial experimental designs, the parameters with the largest effects on the process performance were determined to be pH and organic/aqueous (O/A) ratio for preloading, nickel loading and O/A ratio for extraction, and H_2SO_4 concentration and O/A ratio for stripping. These variables were evaluated in further batch experiments to determine conditions that would allow the production of a high purity nickel sulphate solution and selective stripping of cobalt and iron from the organic phase, and the batch tests results were validated by performing continuous tests on a laboratory scale mixer-settler setup. A flow sheet that allows the production of refined nickel sulphate and cobalt sulphate solutions by extraction with nickel preloaded Cyanex 272 and selective stripping has been proposed. Regeneration of the organic phase is achieved by stripping with 1 M sulphuric acid, which yields an iron containing aqueous stream as effluent.

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1. Introduction

The traditional processing of Ni–Cu sulphide flotation concentrates or Platinum Group Metal (PGM) metal concentrates is via smelting to produce furnace matte, converting of the matte to a low-iron (<7%) converter matte and subsequent leaching of the converter matte using spent electrowinning electrolyte, sometimes in conjunction with additional sulphuric acid. In the PGM industry such as at Western Platinum Limited, Northam Platinum, Zimplats and at Impala Platinum Limited, a modified Sherrit® process is used in a Base Metals Refinery (BMR) to produce a crude $NiSO_4$ solution and partially leached matte, of which the reactions are strongly dependent on iron endpoint and consequently matte mineralogy (Van Schalkwyk et al., 2011; Thyse et al., 2011). The partial dissolution of matte is accompanied with Cu precipitation from spent elec-

trolyte based on cementation and metathesis reactions, during which most of the Ni, Co and Fe and some S dissolve, leaving a solid residue and a crude $NiSO_4$ solution. The solids residue from the first stage leach is sent to the second stage pressure leach (Dorfling et al., 2011), while the nickel sulphate is crystallised from the solution for the recovery of nickel sulphate as $NiSO_4·6H_2O$. Of particular concern for this study is the cobalt and iron that report to the nickel sulphate solution. The objective of this study is hence to evaluate solvent extraction as an option to remove cobalt and iron from the nickel sulphate solution in order to allow the production of a higher purity nickel product and to produce $CoSO_4$ solution as potential by-product without addition of extraneous elements to control pH that would influence the $NiSO_4$ purity.

The separation of cobalt and nickel had traditionally presented problems due to their similar chemical and physical properties. Effective separation of these species only became feasible after the development of a range of phosphorous-based reagents specifically designed for solvent extraction. Of the extractants that have been used for cobalt and nickel separation, phosphoric acids (DEPHA) are the least effective, followed by phosphonic acids (e.g. PC-88A) and phosphinic acids (Cyanex 272) (Devi et al., 1998; Flett, 2005). As a result, Cyanex 272 was chosen as the extractant to be investi-

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gated in the current study. The extraction achieved with Cyanex 272 is highly dependent on pH, with higher extraction typically being achieved as the pH is increased. This pH dependence of the extraction allows separation of metal ions in solution, since the pH at which dissolved metals are extracted from the aqueous phase to the organic phase depends on the type of metal under consideration. Metal ions that have a higher tendency to exchange for hydrogen ions can be extracted at lower pH values than metal ions with a lower tendency to replace hydrogen ions in the organic phase. The majority of solvent extraction processes therefore use a base like NaOH to control the solution pH, which results in the addition of sodium to the purified process solution, as shown in reaction (1) (Nogueira et al., 2009). M^{n+} is an n-valent metal cation, AH is a hydrocarbon (extractant) with proton H and subscripts "org" and "aq" refer to the organic and aqueous phases, respectively.

$$[M^{n+}]_{aq} + n[AH]_{org} + n[NaOH]_{aq} \leftrightarrow [MA_n]_{org} + n[H_2O] + n[Na^+]_{aq} \quad (1)$$
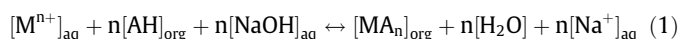
For this particular application, the introduction of sodium to the nickel sulphate solution would negatively affect the quality of the final nickel product. A further potential problem that may arise from the usage of sodium hydroxide involves the formation of sodium-jarosite (according to reaction (2)) if ferric iron is present in the leach solution. Jarosite can form between pH 1 and pH 3 and at temperatures between 20 °C and 200 °C, while goethite formation becomes more prominent at higher pH values (Ismael and Carvalho, 2003; Casas et al., 2007). Iron is one of the major elements responsible for crud formation; the presence of solid jarosite precipitate, in this particular solvent extraction application, will result in crud formation and subsequent valuable metal and organic losses (Ritcey, 1980, 1986).

$$3Fe^{3+} + Na^+ + 2SO_4^{2-} + 6H_2O \leftrightarrow Na[Fe_3(SO_4)_2(OH)_6] + 6H^+ \quad (2)$$
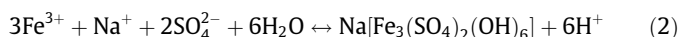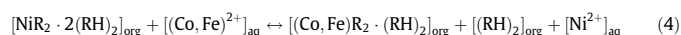
An alternative approach to achieve Ni and Co separation, as proposed by Nogueira et al. (2009) for Cd, Co, and Ni separation, is to preload the Cyanex 272 with nickel by contacting the Cyanex 272 with a nickel sulphate solution to yield nickel loaded Cyanex 272 (Ni-Cyanex 272) prior to extraction of the cobalt and iron. In the preloading stage, the hydrogen ions on the Cyanex 272 are exchanged for nickel ions according to reaction (3):

$$[Ni^{2+}]_{aq} + 3[(RH)_2]_{org} + 2[NaOH]_{aq} \leftrightarrow [NiR_2.2(RH)_2]_{org} + 2[H_2O]_{aq} + 2[Na^+]_{aq} \quad (3)$$

Nickel, cobalt and iron are typically extracted from sulphate solutions in the pH ranges 7–8, 5–6 and 2–3, respectively, with Cyanex 272 (Habashi, 1999). This indicates that, of these metals, iron has the highest tendency to report to the organic phase, while

nickel has the highest tendency to remain in the aqueous phase. The published pH dependence of extraction of different metal species from sulphate solutions with Cyanex 272 (Habashi, 1999) also allows the qualitative prediction of the solvent extraction behaviour of trace amounts of dissolved metals other than Ni, Co, and Fe that might be present in the nickel sulphate leach solution. Zinc and copper, for example, are both extracted at pH values between that of iron and cobalt, with copper expected to follow cobalt in the extraction circuit, while zinc will behave similarly to the dissolved iron. O'Callaghan and Chamberlain (2002) reported that metals extracted at lower pH values will replace metals extracted at higher pH values on the organic phase. If Ni-Cyanex 272 is brought in contact with the nickel sulphate leach solution, the iron and cobalt ions would hence be exchanged for the nickel that has been loaded onto the organic phase, as indicated by reaction (4):

$$[NiR_2 \cdot 2(RH)_2]_{org} + [(Co, Fe)^{2+}]_{aq} \leftrightarrow [(Co, Fe)R_2 \cdot (RH)_2]_{org} + [(RH)_2]_{org} + [Ni^{2+}]_{aq} \quad (4)$$

Since reaction (4) does not involve the exchange of hydrogen ions, the extraction reactions associated with the use of Ni-Cyanex 272 are less dependent on pH and are not characterised by significant changes in the pH during extraction, as was the case when using pure Cyanex 272. For this reason, the addition of a base such as NaOH to the process solution extraction stage is no longer required, and sodium contamination of the nickel sulphate product solution can therefore be avoided. Olivier et al. (2011) compared the sodium additions to the nickel production solution when using pure Cyanex 272 and when using Ni-Cyanex 272 to extract 1 g/l cobalt and 3 g/l iron from a nickel sulphate solution containing 80 g/l nickel. For 95% cobalt and iron extraction, only 0.05 g/l of sodium reported to the nickel product solution when using Ni-Cyanex 272 compared to 4 g/l when using pure Cyanex 272.

Since cobalt and iron are extracted at different pH values, it was believed that separation of these two species by selective stripping would be possible. A weaker acid would be used in the first stripping stage to remove cobalt from the organic phase, followed by a second stripping stage utilising a stronger acid to strip iron. Flett (2005) reported that cobalt can selectively be stripped from co-extracted iron or zinc with 150 g/l H_2SO_4 in Cyanex 272.

A potential process flow sheet based on the discussion above is shown in Fig. 1. There is a limited amount of literature available regarding the use of Ni-Cyanex 272 to remove cobalt and iron from a pregnant nickel sulphate leach solution followed by selective stripping of the extracted metals. The main focus of the study was hence the development of a process flow sheet with appropriate operating conditions to utilise nickel loaded Cyanex 272 to extract 1 g/l cobalt and 3 g/l iron from the nickel sulphate leach
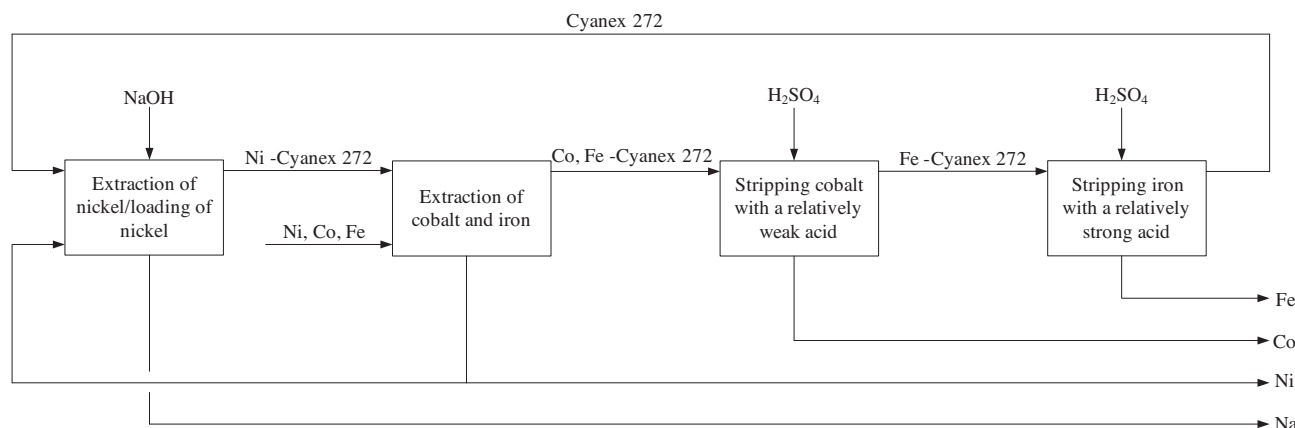

Fig. 1. Flow sheet illustrating the process proposed for removal of cobalt and iron from a nickel sulphate leach solution using solvent extraction with Ni-Cyanex 272 as extractant.

solution containing 80 g/l nickel, followed by separation of cobalt and iron through selective stripping of these species using sulphuric acid. In order to achieve this, batch experiments were conducted to evaluate the effects that different process variables have on the extraction kinetics and equilibrium conditions in the respective stages of the process. The operating conditions that were proposed based on the batch tests were validated by performing continuous tests at the said conditions.

2. Batch tests

2.1. Material and methods

2.1.1. Apparatus and solution preparation

$CoSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ (all CP grade) and H_2SO_4 (98% AR) were supplied by KIMIX South Africa. Cyanex 272 was supplied by Cytec Inc. and was used without further purification. The active component of Cyanex 272 is bis(2,4,4-trimethylpentyl)phosphinic acid and constitutes 85% of Cyanex 272 (Hubicki and Hubicka, 1996). Hence a 10 V% solution of Cyanex 272 in a particular diluent represents a 0.27 M solution of bis(2,4,4-trimethylpentyl)phosphinic acid and a 20 V% Cyanex 272 solution represents a 0.54 M solution of bis(2,4,4-trimethylpentyl)phosphinic acid. It has been reported that Cyanex 272 should not be used under conditions where the ligand is loaded to higher than 60% of its total capacity, since this causes an increase in organic phase viscosity resulting in poor phase separation (Devi et al., 1994; O'Callaghan and Chamberlain, 2002).

The experimental work was performed using synthetic aqueous solutions, made up by dissolving the abovementioned salts in distilled water. The concentration of Cyanex 272 required in the organic phase was dependent on the concentration of the metal species to be extracted. The same basic experimental procedure was followed for the preloading, extraction, and stripping tests. During preloading, Cyanex 272 was brought in contact with a pure nickel sulphate solution; for extraction, the Ni-Cyanex 272 was used for extraction of cobalt and iron from the synthetic process solution, and stripping of the loaded organic phase containing cobalt and iron was achieved by contacting it with sulphuric acid. The aqueous and organic solutions were firstly preheated to the desired operating temperature by using a water heating bath before transferring the appropriate amounts of the respective phases to glass beakers which served as mixing reactors. Magnetic stirrer hotplates were used for mixing of the phases and to control the temperature during agitation. A sodium hydroxide solution was added to adjust the pH of the solution during agitation, as required for the nickel preloading step. After agitation, the pH of the aqueous-organic dispersion was measured before transferring it to 500 ml separation funnels, allowing the two phases to separate. The aqueous phases collected from the separation funnels were diluted to the concentration range required for analysis by atomic absorption spectroscopy (AAS). The metal content in the organic phase was determined by means of mass balances.

2.1.2. Experimental plan

2.1.2.1. Preloading and extraction.
The first set of experiments was performed to determine the minimum agitation time required for phase equilibrium to be achieved in the preloading and extraction stage, respectively. All these experiments were performed using a 20 V% Cyanex 272 solution at an O/A ratio of 1:1 (20 ml organic phase/20 ml aqueous phase) and a temperature of 50 °C. For the preloading kinetic tests, a nickel sulphate solution containing 10.75 g/l nickel was contacted with the organic phase; 1 ml of 3 M NaOH was added to adjust the pH for one series of experiments, while a second series of experiments was performed adding 2 ml

of the 3 M NaOH solution. Sample analyses were performed for tests that had agitation times of 20, 40, 60, 80, 100, 150, 200, 250 and 300 s, respectively, for both series of experiments. For the extraction kinetic tests, two series of experiments were performed using kerosene as diluent and two series of experiments were performed using Shellsol D70 as diluent. For the two series of experiments using kerosene as diluent, the nickel loading of the organic phase was 4.09 g/l and 8.48 g/l, respectively, while the two series of experiments using Shellsol D70 as diluent had organic nickel loadings of 2.47 g/l and 4.66 g/l, respectively. In all four series of experiments, the organic phase was contacted with the synthetic aqueous solution containing 1.07 g/l cobalt, 3.3 g/l iron, and 83.3 g/l nickel; sample analyses were performed for tests that had agitation times of 20, 40, 60, 100, 150 and 300 s, respectively.

Once the minimum agitation time required for phase equilibrium had been determined, experiments were performed according to a 2^4 factorial design for both the preloading and extraction stages to identify the process parameters that have the largest effects on the process performance. For the preloading experiments, the effects that O/A ratio, Cyanex 272 concentration, NaOH addition, and temperature have on the pH and on the nickel loading of the organic phase were investigated. The aqueous phase used to preload the organic phase had an initial nickel content of 9.76 g/l. For the extraction experiments, the effects that O/A ratio, Cyanex 272 concentration, nickel loading of the organic phase, and temperature have on the pH, on cobalt extraction, and on iron extraction were investigated. The full sets of experiments that were performed for the preloading and the extraction stages, together with the high and low values of the respective process parameters, are summarised in Table 1.

Based on the results obtained with the batch tests described above, optimisation tests for the extraction stage were performed using a 20 V% Cyanex 272 solution at a temperature of 50 °C. The O/A ratio was varied between 0.25, 0.5, 0.75, 1, 1.5, 2, 2.5 and 3 with nickel loadings of 0.56, 1.97, 2.94, 3.95, 4.69 and 5.73 g/l at each O/A ratio. Once the optimum O/A ratio and nickel loading for the extraction stage had been selected, the optimisation tests for the preloading stage were performed, again using 20 V% Cyanex 272 at a temperature of 50 °C. The aqueous phase used for preloading contained 80 g/l Ni in order to avoid having to dilute the recycled portion of the nickel sulphate product stream. As a result, high O/A ratios of 26.67, 20, 16, and 13.33 were tested with 3 M NaOH addition amounts of 2.5, 3, 4, 5, 5.5, and 6 ml at each O/A ratio.

2.1.2.2. Stripping.
For the stripping tests, the first set of experiments was also performed to determine the minimum agitation time required to achieve phase equilibrium. All these experiments were performed using an organic phase containing 4.5 g/l Ni, 1 g/l Co, and 3 g/l Fe, at an A/O ratio of 1:1 and a temperature of 50 °C. One series of tests were performed using 0.1 M sulphuric acid as stripping agent, and a second series of experiments used 0.5 M sulphuric acid. For both series of experiments, samples taken after agitating for 0.5, 1, 5, 7, 10, and 15 min, respectively, were analysed.

Next, experiments were performed according to a 2^4 factorial design to determine the effects that A/O ratio, acid concentration, temperature, and the metal content of the organic phase have on the percentage metal stripped. The objective of these experiments was to indentify the process parameters with the largest effects on the process performance. The full set of experiments that were performed are summarised in Table 2, together with the high and low values for the respective process parameters.

In addition to the factorial design batch tests, optimisation tests were performed to evaluate the possibility to separate cobalt and iron by means of selective stripping, and to determine the conditions at which the regeneration of the organic phase would be sufficient for it to be recycled to the preloading stage. These tests were

Table 1
Experimental design as well as high and low values for the preloading and extraction tests.

Run	O/A ratio		Extractant concentration (V%)	3 M NaOH addition (ml)	Temperature (°C)
	ml organic	ml aqueous			
Preloading					
1	40	20	10	1	30
2	10	20	10	1	30
3	40	20	20	1	30
4	10	20	20	1	30
5	40	20	10	2	30
6	10	20	10	2	30
7	40	20	20	2	30
8	10	20	20	2	30
9	40	20	10	1	60
10	10	20	10	1	60
11	40	20	20	1	60
12	10	20	20	1	60
13	40	20	10	2	60
14	10	20	10	2	60
15	40	20	20	2	60
16	10	20	20	2	60

Run	O/A ratio		Extractant concentration (V%)	Ni loading (g/l)	Temperature (°C)
	ml organic	ml aqueous			
Extraction					
1	40	20	10	2.83	30
2	10	20	10	2.83	30
3	40	20	20	2.47	30
4	10	20	20	2.47	30
5	40	20	10	4.76	30
6	10	20	10	4.76	30
7	40	20	20	4.66	30
8	10	20	20	4.66	30
9	40	20	10	2.83	60
10	10	20	10	2.83	60
11	40	20	20	2.47	60
12	10	20	20	2.47	60
13	40	20	10	4.76	60
14	10	20	10	4.76	60
15	40	20	20	4.66	60
16	10	20	20	4.66	60

Table 2
Experimental design as well as high and low values for the stripping tests.

Run	O/A ratio		Acid concentration (M)	Metal loading (g/l Ni, Co, Fe)	Temperature (°C)
	ml organic	ml aqueous			
1	20	40	0.1	2.26, 0.52, 1.58	30
2	20	10	0.1	2.26, 0.52, 1.58	30
3	20	40	0.5	2.26, 0.52, 1.58	30
4	20	10	0.5	2.26, 0.52, 1.58	30
5	20	40	0.1	4.67, 1.03, 3.14	30
6	20	10	0.1	4.67, 1.03, 3.14	30
7	20	40	0.5	4.67, 1.03, 3.14	30
8	20	10	0.5	4.67, 1.03, 3.14	30
9	20	40	0.1	2.26, 0.52, 1.58	60
10	20	10	0.1	2.26, 0.52, 1.58	60
11	20	40	0.5	2.26, 0.52, 1.58	60
12	20	10	0.5	2.26, 0.52, 1.58	60
13	20	40	0.1	4.67, 1.03, 3.14	60
14	20	10	0.1	4.67, 1.03, 3.14	60
15	20	40	0.5	4.67, 1.03, 3.14	60
16	20	10	0.5	4.67, 1.03, 3.14	60

performed at a temperature of 50 °C, using an organic phase containing 0.75 g/l cobalt, 2.1 g/l iron, and 2.7 g/l nickel (these concentrations were determined based on the proposed operating conditions for the preloading and extraction stages). The A/O ratio was varied between 0.5, 0.75, 1, 1.5, 2.25 and 3 with H_2SO_4 concentrations of 0.025, 0.05, 0.075, 0.1, 0.25, 0.5, 0.75, 1, 2, and 4 M at each A/O ratio.

2.2. Results and discussion

2.2.1. Preloading and extraction
2.2.1.1. Kinetics. During preloading, the nickel that reports to the organic phase at equilibrium conditions is extracted almost instantaneously, with less than 20 s of agitation required for the phase equilibrium conditions to be achieved, as shown in Fig. 2.

Concerning the kinetics of the extraction stage, it can be seen from Fig. 3c and d that the agitation time required to achieve equilibrium cobalt and iron extraction decreases as the nickel loading of the organic phase increases. This suggests that the kinetics of the extraction reactions can be described by conventional concentration dependent rate laws. It was observed that, especially for low nickel loadings, the cobalt extraction initially increases before starting to decrease again (Fig. 3c). This indicates that cobalt and iron extraction occur simultaneously during the initial stages of the extraction process according to reaction (4), and that the rates of cobalt and iron extraction are comparable when the nickel loading of the organic phase is sufficiently high. Referring back to Section 1, it is known that iron can be extracted at the lowest pH and has the highest tendency to report to the organic phase, followed by cobalt, and lastly nickel. Therefore, if the organic phase initially contained too little nickel to be exchanged for all the iron and cobalt, the iron will be extracted to the organic phase by exchange with the cobalt present on the organic phase as soon as the available nickel has been depleted. This will cause the cobalt concentration in the aqueous phase to start increasing again. If the pH is high enough at the point where nickel becomes depleted, iron will also be
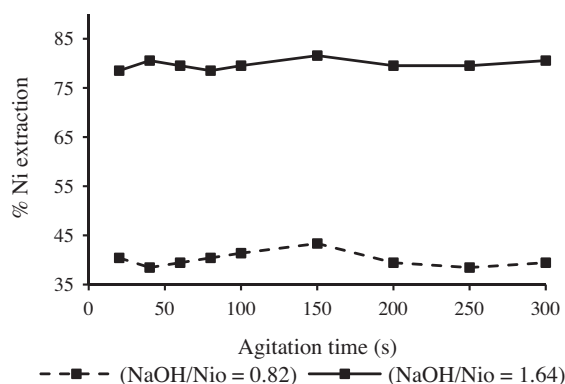
Fig. 2. % Ni extracted with Cyanex 272 during preloading as a function of agitation time.

extracted by exchange with the hydrogen ions on the organic phase (according to reaction (1)), which explains the more significant decrease in pH for the organic phases with a lower initial nickel loading, as shown in Fig. 3a. When using a high nickel loading (8.48 g/l), there was sufficient nickel in the organic phase to be exchanged for both cobalt and iron. The drop in pH observed for this nickel loading essentially occurred after all the iron and cobalt had been extracted, and can be attributed to the fact that the pH after iron and cobalt extraction had occurred was still high enough for noticeable nickel

extraction from the aqueous phase to the organic phase to occur. This is also illustrated in Fig. 3b, where the most noticeable increase in nickel extraction over time was observed for the highest nickel loading. It was concluded that an agitation time of 5 min would be sufficient to achieve phase equilibrium when using a sufficiently high nickel loading on the organic phase was utilised. This agitation time compares well with the agitation time recommended in previous studies utilising Cyanex 272 for metal extraction (Rodrigues and Mansur, 2009; Park and Mohapatra, 2006; Bhaskara Sarma and Reddy, 2002).

2.2.1.2. Factorial design. A significance level of 0.05 was selected for interpretation of the *p*-value results obtained by performing regression analyses for the experiments performed according to the factorial design. Referring to Table 3, in can be seen that the O/A ratio and NaOH addition are the factors that have a statistically significant effect on the Ni loading of the organic phase, while all the tested factors except temperature have a statistically significant influence on the pH. Given the fact that the Ni loading is the process variable of primary interest, it was decided to perform the optimisation preloading tests at a constant temperature of 50 °C with a 20 V% Cyanex 272 solution.

For the extraction tests, all the variables except the extractant concentration were found to have a statistically significant effect on both the cobalt extraction and iron extraction, as shown in Table 4. Given the limited effect of the extractant concentration on the extraction achieved, the extractant concentration was not
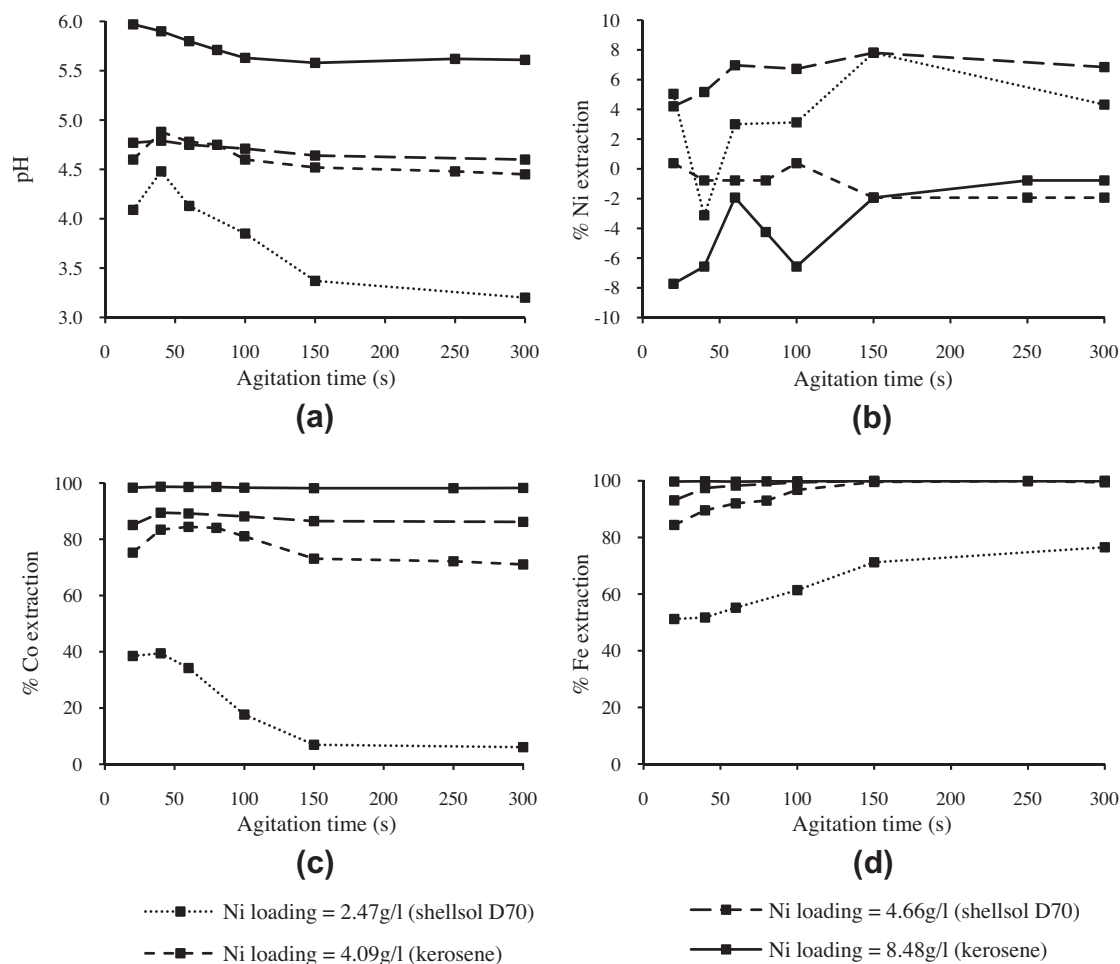

Fig. 3. Process parameters illustrated as a function of agitation time and Ni loading, when using Ni-Cyanex 272 as extractant: (a) pH, (b) percentage nickel extraction, (c) percentage cobalt extraction, and (d) percentage iron extraction.

Table 3
Calculated *p*-values for preloading tests with Ni loading and pH as response variables.

Variable	$y = z_o + z_1a + z_2b + z_3c + z_4d$	
	Ni loading (g/l)	pH
O/A ratio (a)	6.00E−22	5.00E−24
Extractant concentration (b)	0.68	6.00E−15
NaOH addition (c)	3.00E−13	6.00E−24
Temperature (d)	0.9	0.08

Table 4
Calculated *p*-values for extraction tests with Co and Fe extraction as response variables.

Variable	$y = z_o + z_1a + z_2b + z_3c + z_4d$	
	Co extraction (%)	Fe extraction (%)
O/A ratio (a)	5.00E−40	3.00E−20
Extractant concentration (b)	0.572	0.604
Ni loading (c)	3.00E−06	5.00E−07
Temperature (d)	0.006	0.03

varied during the optimisation extraction experiments. A 20 V% Cyanex 272 solution rather than a 10 V% solution was used for subsequent tests because it allows reduced O/A ratios to be used and it reduces the probability of phase separation problems occurring as a result of overloading. As a result of poor phase separation observed for various tests performed at 25 °C, it was also decided to perform the optimisation tests at a constant temperature of 50 °C.

2.2.1.3. O/A ratio and nickel-loading (Co and Fe extraction). Considering the discussion in Section 2.2.1.2, the nickel loading of the organic phase and the O/A ratio were the two factors that were varied in the extraction optimisation tests. The nickel loading and O/A ratio requirements for the extraction section were determined prior to the preloading optimisation tests.

Fig. 4 shows the typical nickel losses from the nickel sulphate process solution as well as the sodium additions to the purified nickel sulphate stream after extraction at the different operation conditions. Negative extraction of nickel, as observed in Fig. 4a, implies that more nickel was transferred from the Ni-Cyanex 272 to

the aqueous phase than from the aqueous process solution to the organic phase. Except for extraction performed using a nickel loading of 0.56 g/l at an O/A ratio of 2, the nickel lost from the process solution to the organic phase did not exceed 6%. In general, the sodium additions to the purified nickel stream increased as the nickel loading increased for O/A ratios larger than 1 (Fig. 4b). This is because more NaOH must be added during the preloading stage in order to obtain higher nickel loadings, which subsequently increases the probability of sodium uptake by the extractant and ultimately higher sodium additions to the purified nickel sulphate solution. Similarly, when the O/A ratio is increased the absolute amount of sodium entering the extraction system on the preloaded Cyanex 272 increases, which increases the probability of sodium uptake by the extractant. The negative sodium additions are due to impure sodium that was in the salts used to prepare the synthetic representation of the pregnant nickel leach solution which was then also extracted onto the organic.

When an organic phase with a higher nickel loading is used, the O/A ratio required for cobalt and iron extraction decreases (see Fig. 5a and c). It can hence be concluded that the extraction is largely dependent on the nickel content of the organic phase. This set of data confirms that, if limited nickel is available to be exchanged for Co and Fe, the Fe would preferentially be extracted. For the Ni loading of 1.97 g/l, for example, the Fe extraction increases gradually as the O/A ratio is increased until the total Ni present in the organic phase is sufficient to achieve Fe extraction close to 100%, which occurs at an O/A ratio of 1.5. It is only at O/A ratios higher than 1.5, when Ni is available in excess of what is required for Fe extraction, that significant (>10%) Co extraction is achieved. Fig. 5e illustrates the fact that hydrogen ions on the organic are exchanged for cobalt and iron, particularly so when the nickel on the organic has been depleted, as long as the pH remains high enough. At low O/A loadings, a small amount of nickel is available to be exchanged and, consequently, iron is exchanged for hydrogen on the organic which leads to a decrease in the pH. Despite this exchange reaction taking place, the iron extraction did not exceed 50% for any of the nickel loadings at an O/A ratio of 0.25 because the pH fell too low before more Fe could be extracted. For all the O/A ratios larger than 1, the highest nickel loading resulted in the highest pH because less hydrogen had to be exchanged for Fe and Co. Based on the above findings, it is suggested that the extraction stage be
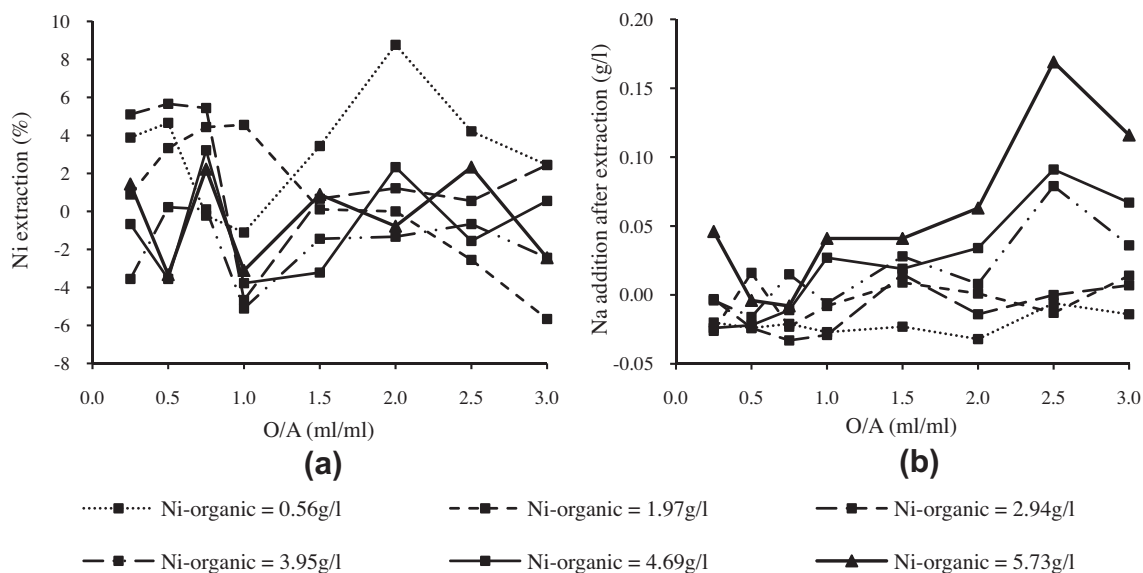

Fig. 4. 80 g/l nickel extraction from (a) and sodium addition to (b) the product solution after extraction as a function of nickel loading and O/A ratio.
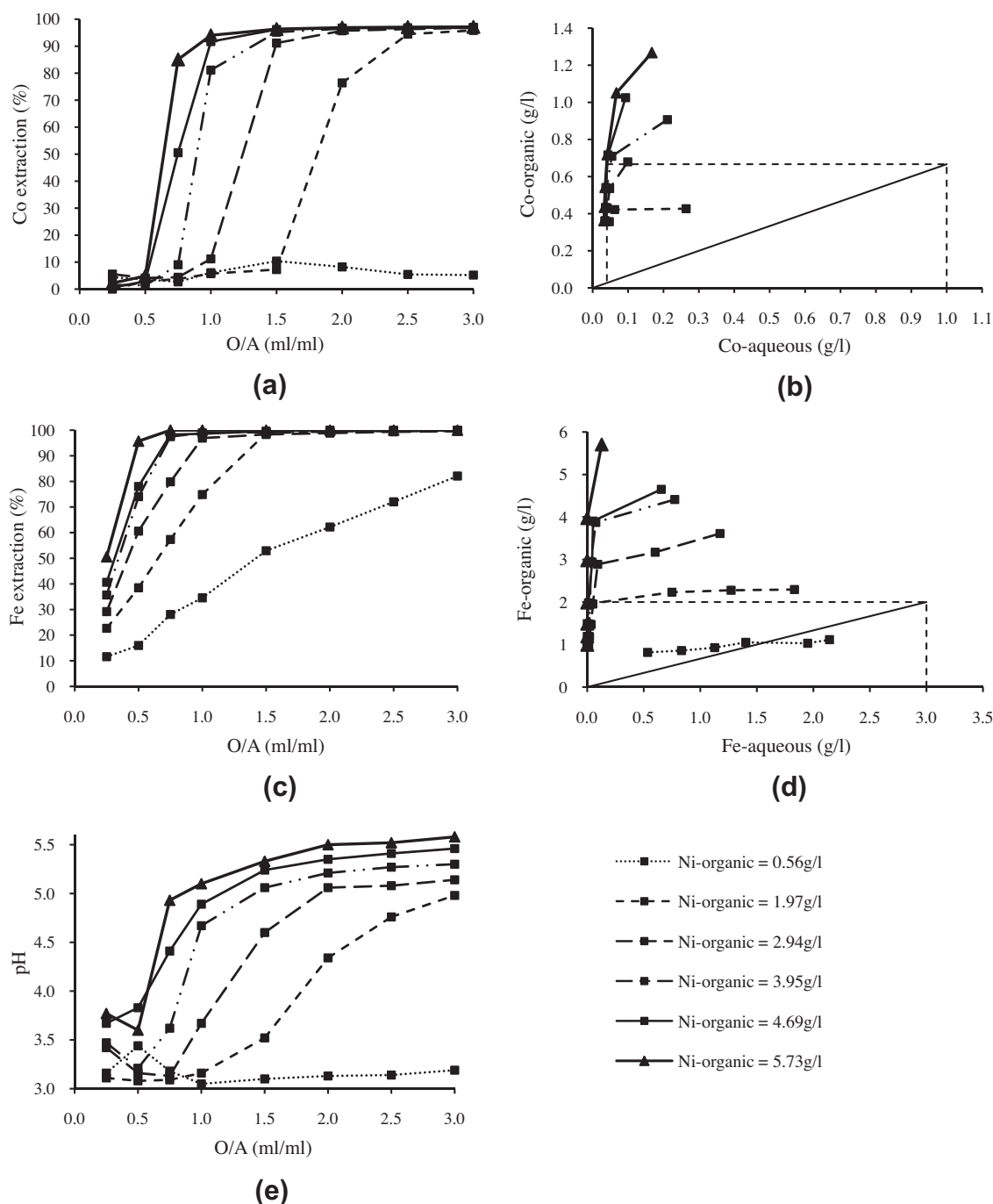
Fig. 5. Process parameters as a function of O/A ratio and nickel loading: (a) percentage cobalt extraction, (b) cobalt extraction isotherm, (c) percentage iron extraction, (d) iron extraction isotherm, and (e) pH.

operated at an O/A ratio of 1.5 with a nickel loading between 2.95 g/l and 3.95 g/l to give maximum cobalt (95–96%) and iron (99–100%) extraction. This O/A ratio is sufficiently high to avoid ligand overloading, while the nickel loading is relatively low which reduces the quantity of nickel that has to be recycled from the purified product solution. The McCabe–Thiele diagrams in Fig. 5b and d illustrate that the abovementioned extraction percentages are possible at the proposed conditions using a single stage. Considering the amount of loaded nickel on the organic phase relative to the impurity content of the aqueous phase, these results are comparable with the results presented by O'Callaghan and Chamberlain (2002). In the aforementioned study, it was reported that

a nickel loading of 7.5 g/l can be used at an O/A ratio of 1 to remove more than 98% of the impurities from a nickel sulphate solution containing 71.98 g/l Ni, 6.5 g/l Co, 11 ppm Cu, 5 ppm Zn, and 11 ppm Mn.

2.2.1.4. O/A ratio and pH for nickel preloading. The factors identified as having statistically significant effects on the Ni loading, namely the O/A ratio and pH, were varied in the preloading optimisation tests. If a portion of the purified nickel sulphate stream containing 80 g/l nickel is used to preload Cyanex 272, an O/A ratio between 13.3 and 26.7 has to be used to generate an organic phase containing between 6 g/l Ni and 3 g/l Ni, respectively, assuming that all the

nickel is transferred from the aqueous phase to the organic phase. The preloading results as a function of the O/A ratio and pH are shown in Fig. 6.

From Fig. 6a it can be seen that the O/A ratio does not have a significant influence on extraction at pH values higher than 6.7, while all of the nickel is extracted irrespective of the O/A ratio at a pH higher than 7.2. In order to minimise Ni losses to the aqueous effluent containing predominantly sodium, the preloading stage should be operated at a pH value above approximately 7. At these high pH values, using an O/A ratio close to 26.7 would yield a nickel loading between 2.95 g/l and 3.95 g/l (refer to Fig. 6b), which was proposed as the operating condition for the extraction section. According to Fig. 6c, this extraction would be achieved in a single preloading stage. This relatively high O/A ratio also reduces the portion of the nickel sulphate product solution that has to be recycled for a specific organic phase flow rate.

2.2.2. Stripping

2.2.2.1. Kinetics.
The stripping rates are slower than the preloading and extraction kinetics, with approximately 410 s of agitation required for equilibrium to be achieved, as shown in Fig. 7. Consequently, an agitation period of 600 s was allowed for succeeding stripping tests.

2.2.2.2. Factorial design.
The p-values calculated for the investigated process variables when using percentage nickel stripped, percentage cobalt stripped, and percentage iron stripped as the response variable, respectively, are listed in Table 5. The A/O ratio and the acid concentration were found to have statistically significant effects on the stripping of all three metals investigated. The metal loading on the organic phase was found to have a statistically significant effect on the Ni and Co stripping. However, it was observed that this effect is not unrelated to the acid concentration and A/O ratio; at high metal loadings, the amount of hydrogen ions available to strip the loaded metals from the organic phase was insufficient, hence leading to lower stripping percentages. Given this interaction between the metal loading and the acid concentration and A/O ratio, it was decided not to vary the metal loading of the organic, but to rather perform the stripping tests on an organic representative of the typical organic phase composition expected considering the preloading and extraction conditions proposed previously. Since the effect of temperature on stripping was only statistically significant for Ni stripping, with 5–10% higher stripping achieved at 60 °C than at 30 °C, a temperature of 50 °C was chosen for subsequent stripping experiments.

2.2.2.3. A/O ratio and H_2SO_4 concentration.
Based on the results obtained with the factorial experimental design, the effects of the A/O ratio and H_2SO_4 concentration on stripping were considered in the optimisation tests. Table 6 gives a summary of the ease of phase separation as well as the ratios of percentage extractions achieved at the different combinations of experimental conditions, while
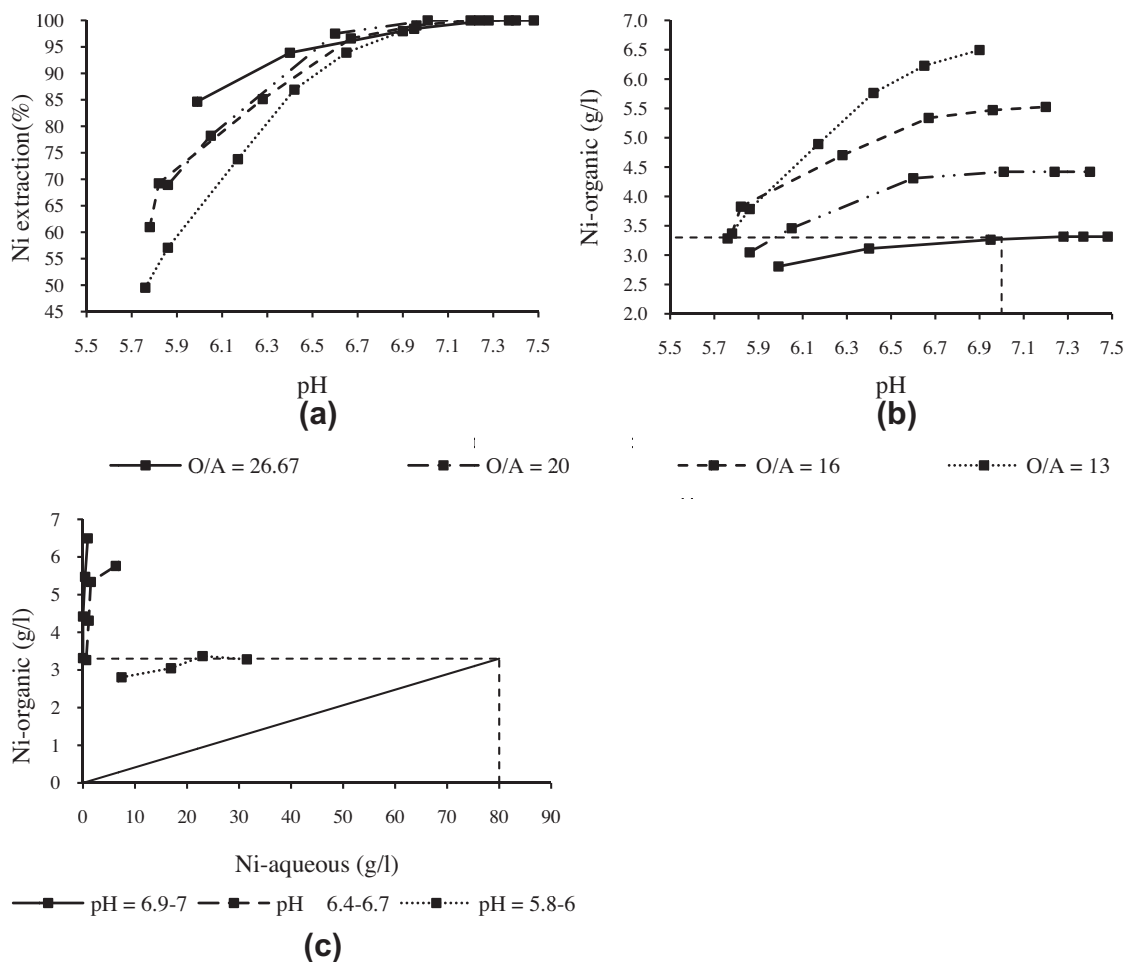

Fig. 6. Percentage nickel extraction during preloading (a), nickel loading of Cyanex 272 (b) and the nickel extraction isotherm (c) as a function of O/A ratio and pH (NaOH addition).
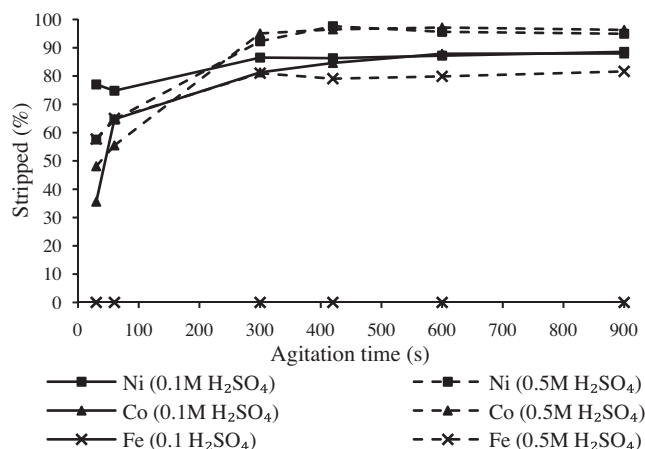
Fig. 7. % Metal stripped from an organic phase loaded with 4.5 g/l nickel, 1.04 g/l cobalt and 2.96 g/l iron as a function of agitation time and stripping agent concentration.

Fig. 8 shows the percentage stripping of the different metals as a function of the acid concentration for different A/O ratios. Stripping increased as the acid concentration and A/O ratio were increased, with nickel being stripped initially, followed by cobalt and then iron. Phase separation proved troublesome under conditions where small amounts of hydrogen ions were available for stripping, as

Table 5
Calculated p-values for stripping tests with Ni, Co, and Fe stripping as response variables.

Variable	$y = z_o + z_1a + z_2b + z_3c + z_4d$ Stripped (%)		
	Ni	Co	Fe
A/O ratio (a)	3.00E−04	2.00E−03	2.00E−06
Acid concentration (b)	2.00E−04	4.00E−04	9.00E−22
Metal loading (c)	7.00E−06	6.00E−05	0.08
Temperature (d)	7.00E−03	0.399	0.911

indicated by the shaded areas in Table 6. Under conditions where good phase separation was achievable, nickel and cobalt could not be stripped selectively, with ratios of percentage extractions varying between 0.92 (using 0.75 M H_2SO_4 at an A/O ratio of 3) and 1.18 (using 0.1 M H_2SO_4 at an A/O ratio of 2.25). As shown in Fig. 8c, virtually no iron stripping was observed when using acid with a concentration of 0.1 M or lower, irrespective of the A/O ratio. This resulted in the infinitely high (indicated by *inf* in Table 6) ratios of percentage extractions for cobalt with respect to iron and for nickel with respect to iron at these conditions. According to Fig. 8a and b, the highest percentage nickel and cobalt stripping under conditions where no iron is stripped can be achieved when using 0.1 M H_2SO_4 at an A/O ratio of 3. Iron stripping of between 93% and 100% was achieved when using 1 M H_2SO_4 at A/O ratios larger than 0.75, which indicates that complete regeneration of the organic phase would be possible.

Table 6
Phase separation and selectivity defined by the relative quantities stripped of each metal.

H_2SO_4 (M)	A/O																	
	0.50			0.75			1.00			1.50			2.25			3.00		
0.025	poor			poor			poor			poor			poor			poor		
	42.79	inf	inf	84.94	Inf	inf	85.8	inf	inf	inf	inf	inf	261.6	inf	inf	1.68	inf	inf
0.05	poor			poor			poor			good			good			good		
	276.8	inf	inf	159.9	inf	inf	1.71	inf	inf	0.99	inf	inf	1.05	inf	inf	1.11	inf	inf
0.075	poor			poor			poor			good			good			good		
	331.6	inf	inf	1.47	inf	inf	1.00	inf	inf	1.02	inf	inf	1.15	inf	inf	1.09	inf	inf
0.1	poor			poor			poor			good			good			good		
	77.89	inf	inf	1.02	inf	inf	1.03	inf	inf	1.06	inf	inf	1.18	inf	inf	1.08	inf	inf
0.25	poor			poor			good			good			good			good		
	1.07	601.91	645.42	1.07	3.27	3.48	1.05	2.32	2.43	1.03	1.93	2.00	1.09	1.94	2.12	1.12	2.04	2.28
0.5	good			good			good			good			good			good		
	1.06	1.40	1.49	1.04	1.19	1.24	1.03	1.14	1.18	1.05	1.15	1.20	1.02	1.20	1.22	1.08	1.21	1.31
0.75	good			good			good			good			good			good		
	1.06	1.24	1.31	1.01	1.11	1.12	0.99	1.12	1.11	1.11	1.04	1.16	0.97	1.20	1.16	0.92	1.30	1.19
1	good			good			good			good			good			good		
	1.03	1.32	1.36	1.01	0.91	0.92	1.00	1.08	1.09	0.98	1.12	1.10	0.99	1.06	1.05	0.95	1.16	1.11
2	good			good			good			good			good			good		
	1.09	1.06	1.15	0.97	1.04	1.01	0.97	1.07	1.04	0.95	1.12	1.06	0.97	1.14	1.11	0.95	1.34	1.28
4	good			good			good			good			good			good		
	1.01	1.01	1.02	0.98	1.02	1.00	0.98	1.11	1.09	0.93	1.17	1.08	0.98	1.20	1.17	0.95	1.26	1.20

Legend for interpretation of table 6:

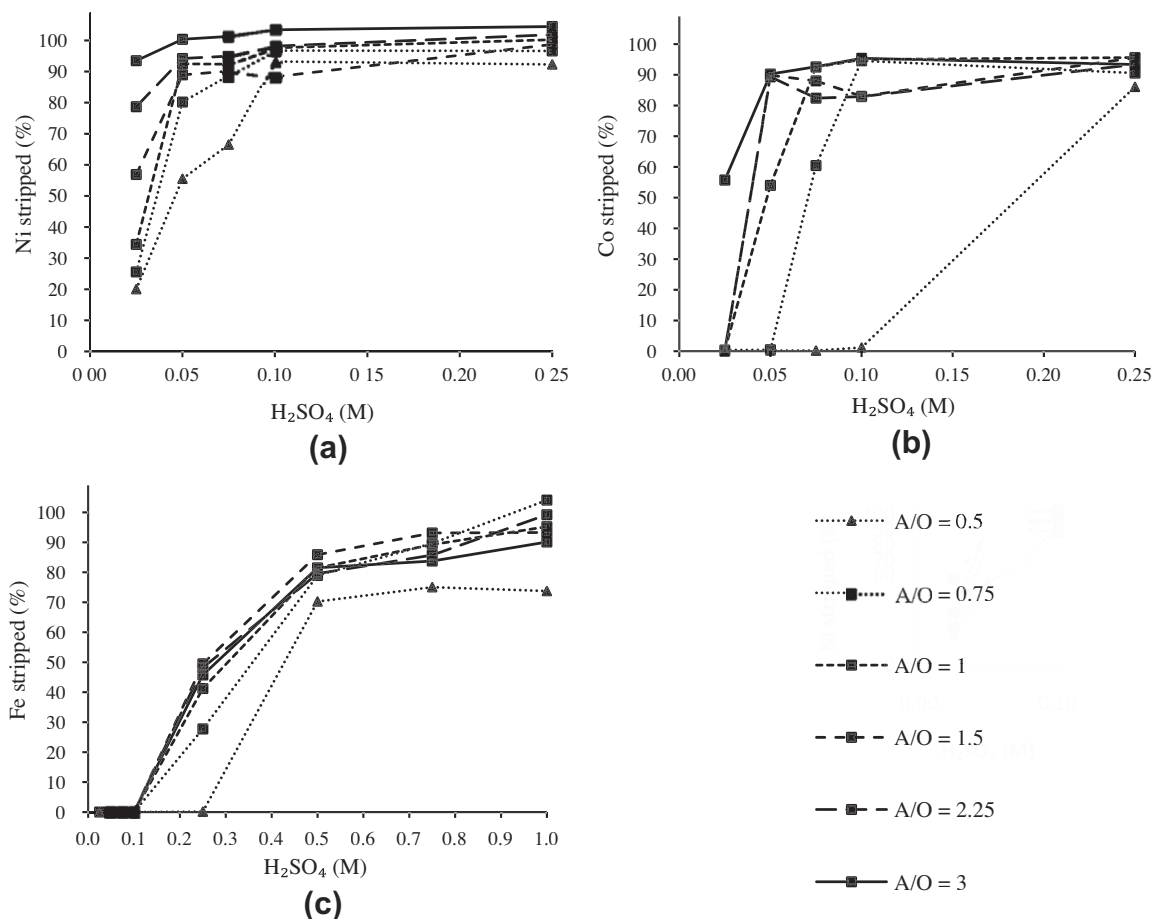| H_2SO_4 (M)	A/O		
	Phase separation		
	$S(\%)_{Ni}/S(\%)_{Co}$	$S(\%)_{Co}/S(\%)_{Fe}$	$S(\%)_{Ni}/S(\%)_{Fe}$

Fig. 8. Percentage metal stripping as a function of H₂SO₄ concentration and A/O ratio: (a) nickel, (b) cobalt, and (c) iron.

3. Continuous tests

A laboratory scale four-stage mixer-settler setup was used to perform continuous tests in order to validate the operating conditions proposed based on the batch tests. Two tests were performed to evaluate the performance of the preloading and extraction stages, followed by two more tests to evaluate the performance of the stripping stage.

3.1. Plant setup and configurations

A four stage mixer-settler plant manufactured by SX Kinetics and consisting of borosilicate glass mixers and settlers with capacities of 320 ml and 1350 ml each, respectively, was used for the tests. Peristaltic pumps with a capacity of 20–200 ml/min were used to feed the organic and aqueous phases to the plant. Four variable speed mixer agitators (40–2000 rpm) with curved blade impellers manufactured from polypropylene were used for agitation in the mixers (a stirring speed of 1000 rpm was used for all the tests). Stainless steel containers with a capacity of seven litres each were used to contain the organic (20 V% Cyanex 272 in Shellsol D70) and aqueous solutions to be fed to the plant. These solutions were preheated by placing the containers in a heating bath set at a temperature of 50 °C. Online temperature and pH probes were used to monitor the operating conditions in each stage; the pH in the preloading stage was controlled by manually adjusting the gravity flow addition rate of a NaOH solution. The O/A ratio at each stage was determined by taking a 10 ml sample from the mixing chamber, and depositing it into a measuring cylinder which revealed the O/A ratio once the two phases separated.

The circuit configuration and operating conditions utilised for the preloading and extraction tests are shown in Figs. 9 and 10. The pump capacities allowed for a maximum O/A ratio of 10 to be achieved, which is lower than the ratio of 25 proposed for the preloading section. Consequently, the preloading section was operated at a lower A/O ratio using an aqueous solution containing less than 80 g/l nickel to produce an organic phase with the desired nickel loading, which allowed the proposed extraction conditions to be validated. The preloading conditions shown in Fig. 9 were used for the first extraction test to produce preloaded Cyanex 272 containing between 3 g/l and 3.5 g/l Ni. In the second extraction test, the preloading operating conditions shown in Fig. 10 were selected to produce an organic phase with a higher nickel loading to investigate the effect it would have on the performance of the extraction stage.

The circuit configuration and operating conditions utilised for the stripping tests are shown in Figs. 11 and 12. The metal loadings of the organic phase were varied between the two tests to investigate the sensitivity of the stripping performance at the proposed conditions to variations in the composition of the organic phase. Except for the iron stripping stage in the first stripping test (Fig. 11), two mixers and settlers made up a single stripping stage in order to allow a longer agitation time for the stripping to reach equilibrium.

3.2. Results and discussion

3.2.1. Preloading and extraction

The parameters indicating the preloading and extraction performance for the two configurations shown in Figs. 9 and 10 are shown in Figs. 13 and 14, respectively.
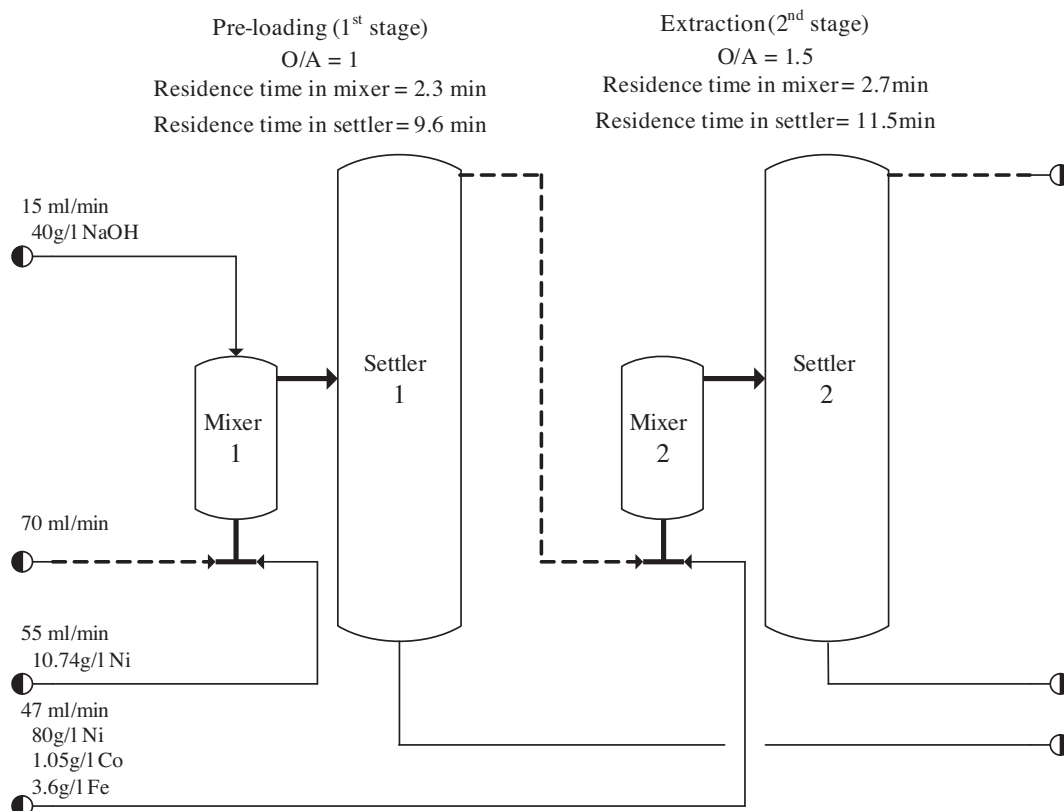
Pre-loading (1st stage)
O/A = 1
Residence time in mixer = 2.3 min
Residence time in settler = 9.6 min

Extraction (2nd stage)
O/A = 1.5
Residence time in mixer = 2.7 min
Residence time in settler = 11.5 min

15 ml/min
40g/l NaOH

70 ml/min

55 ml/min
10.74g/l Ni

47 ml/min
80g/l Ni
1.05g/l Co
3.6g/l Fe

Mixer 1
Settler 1
Mixer 2
Settler 2

Fig. 9. Mixer-settler configuration and operating conditions for preloading and extraction when generating a nickel loading between 3 g/l and 3.5 g/l on the organic phase (dotted lines represent organic streams; solid lines represent aqueous streams).
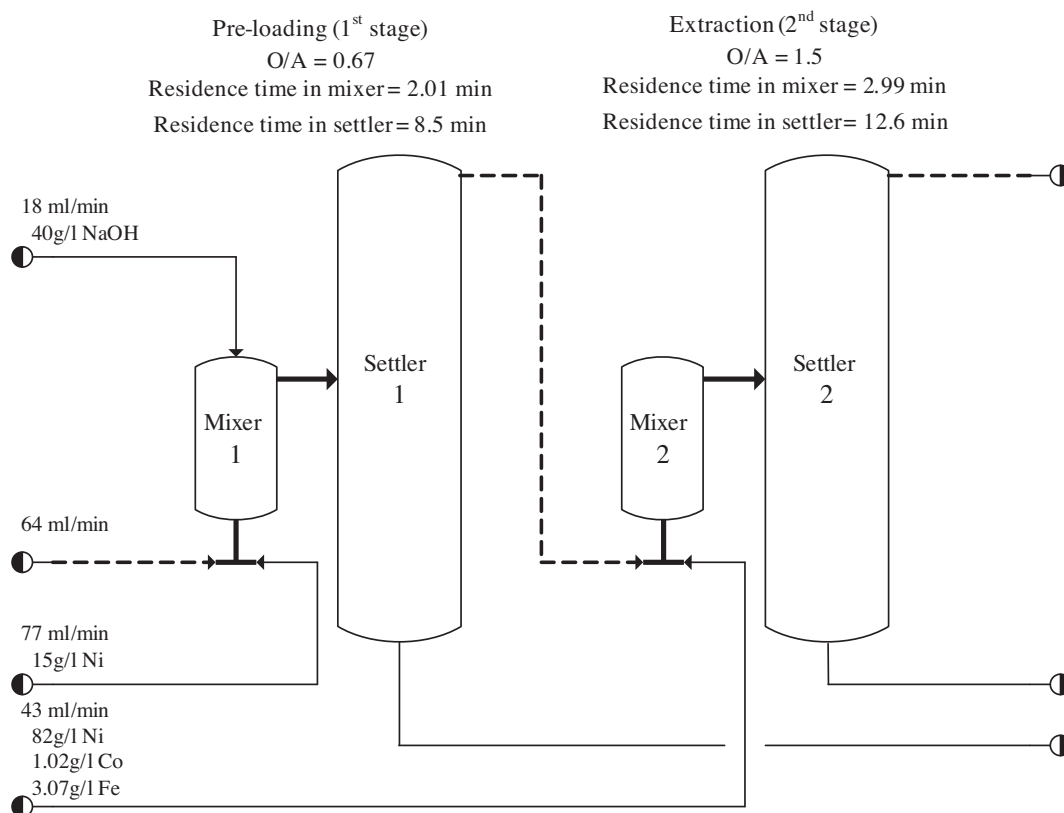
Pre-loading (1st stage)
O/A = 0.67
Residence time in mixer = 2.01 min
Residence time in settler = 8.5 min

Extraction (2nd stage)
O/A = 1.5
Residence time in mixer = 2.99 min
Residence time in settler = 12.6 min

18 ml/min
40g/l NaOH

64 ml/min

77 ml/min
15g/l Ni

43 ml/min
82g/l Ni
1.02g/l Co
3.07g/l Fe

Mixer 1
Settler 1
Mixer 2
Settler 2

Fig. 10. Mixer-settler configuration and operating conditions for preloading and extraction when generating a nickel loading between 4.9 g/l and 5.2 g/l on the organic phase (dotted lines represent organic streams; solid lines represent aqueous streams).

Ni and Co stripping (1st stage)
A/O = 2.3
Residence time in mixers = 3.8min
Residence time in settlers = 16.2min

Fe stripping (2nd stage)
A/O = 0.72
Residence time in mixer = 3.7min
Residence time in settler = 15.7min

50 ml/min
0.94g/l Ni
0.37g/l Co
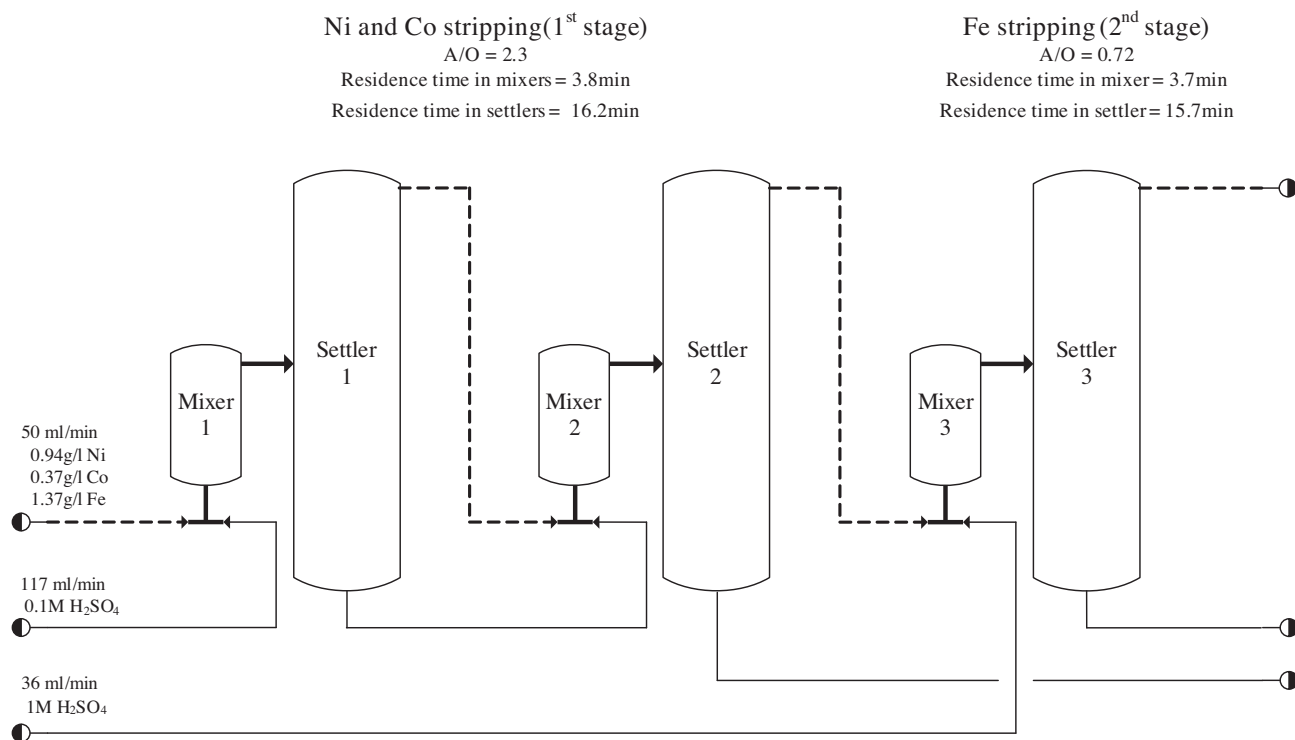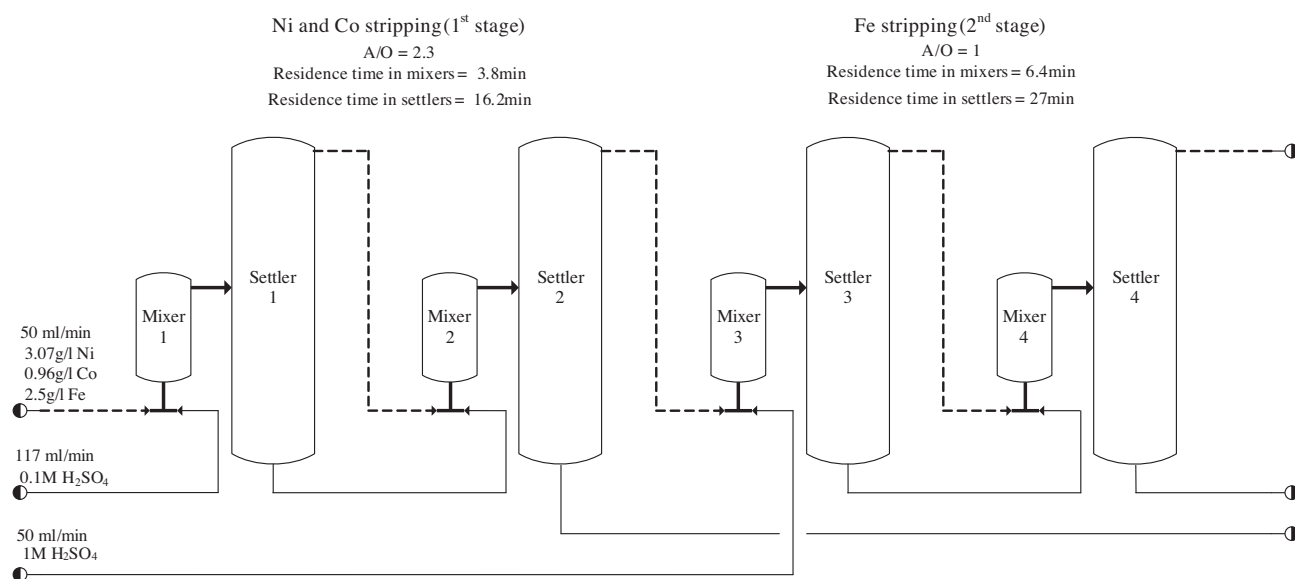1.37g/l Fe

117 ml/min
0.1M H₂SO₄

36 ml/min
1M H₂SO₄

Fig. 11. Mixer-settler configuration and operating conditions for stripping of an organic phase with a lower metal loading (dotted lines represent organic streams; solid lines represent aqueous streams).

Ni and Co stripping (1st stage)
A/O = 2.3
Residence time in mixers = 3.8min
Residence time in settlers = 16.2min

Fe stripping (2nd stage)
A/O = 1
Residence time in mixers = 6.4min
Residence time in settlers = 27min

50 ml/min
3.07g/l Ni
0.96g/l Co
2.5g/l Fe

117 ml/min
0.1M H₂SO₄

50 ml/min
1M H₂SO₄

Fig. 12. Mixer-settler configuration and operating conditions for stripping of an organic phase with a higher metal loading (dotted lines represent organic streams; solid lines represent aqueous streams).

For the results presented in Fig. 13, steady state was reached approximately 85 min after NaOH addition was started. The steady state nickel loading ranged between 3.26 g/l and 3.36 g/l, which is within the range proposed based on the batch tests. The cobalt and iron extractions achieved at steady state were approximately 94.5% and 97.8%, respectively, which confirms that the proposed extraction conditions are sufficiently robust to treat a nickel sulphate leach solution with an iron concentration above 3 g/l.

For the second preloading and extraction test, steady state was reached after approximately 55 min (refer to Fig. 14). At

steady state the nickel loading ranged between 4.98 g/l and 5.16 g/l. The cobalt and iron extractions achieved were approximately 95.5% and 98.5%, respectively. By increasing the organic phase nickel loading from 3.3 g/l to 5.1 g/l, on average, the cobalt and iron extractions were increased by 1% and 0.7% respectively. This relatively small increase in nickel and cobalt extraction will not justify a higher nickel loading, which would entail recycling more of the nickel sulphate product stream and increasing the NaOH addition to the preloading stage. This, in turn, would increase the probability of sodium reporting to
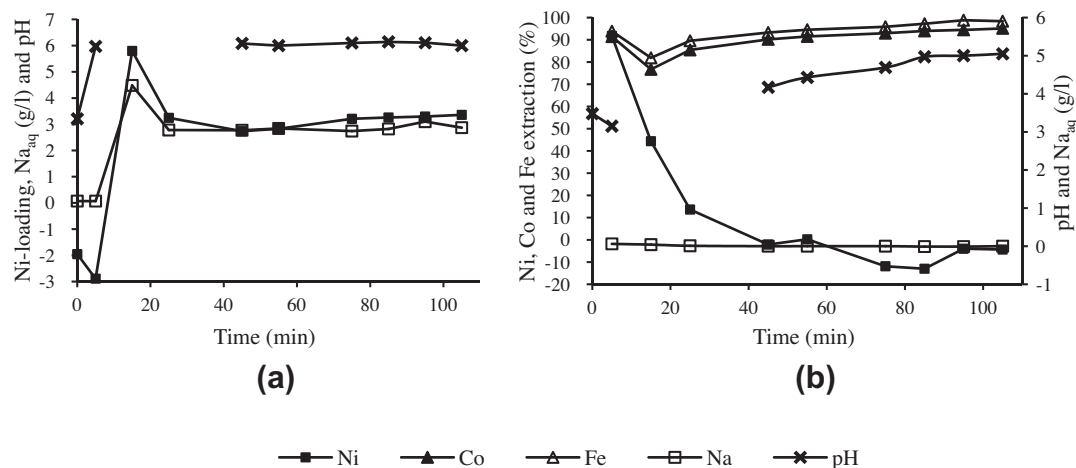
Fig. 13. Continuous test results for preloading (a) and extraction (b) when generating a lower nickel loading on the organic phase (plant configuration in Fig. 9).
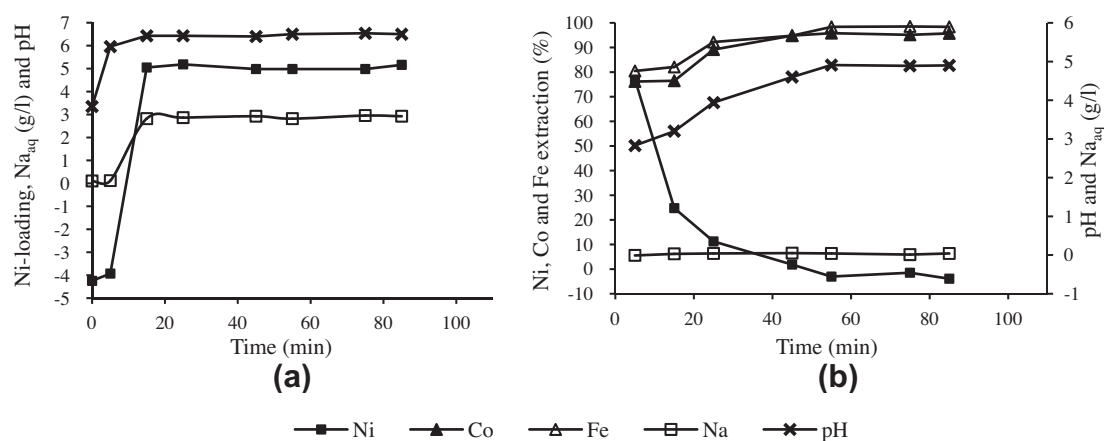

Fig. 14. Continuous test results for preloading (a) and extraction (b) when generating a higher nickel loading on the organic phase (plant configuration in Fig. 10).
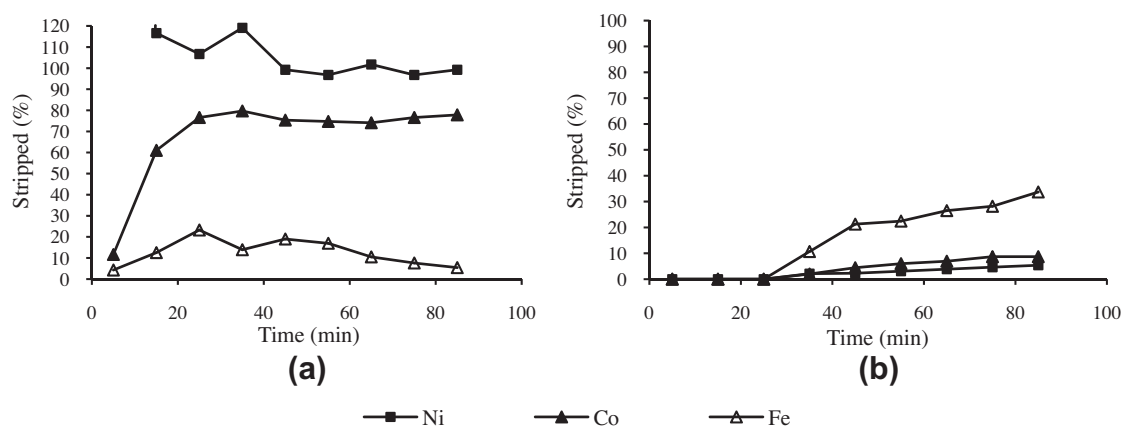

Fig. 15. Continuous test results for stripping of the organic phase with the lower metal loading (plant configuration in Fig. 11); (a) and (b) represent the 1st and 2nd stripping stages, respectively.

the nickel sulphate product solution. From the continuous tests, it was found that virtually no sodium reports to the product stream for the low nickel loading, while the high nickel loading results in a sodium concentration of 0.1–0.4 g/l in the product stream.

3.2.2. Stripping

The percentage nickel, cobalt and iron stripped in both stages for the two configurations shown in Figs. 11 and 12 are shown in Figs. 15 and 16, respectively. The percentages stripped in both stages were calculated with respect the metal loading being fed to the first stage.
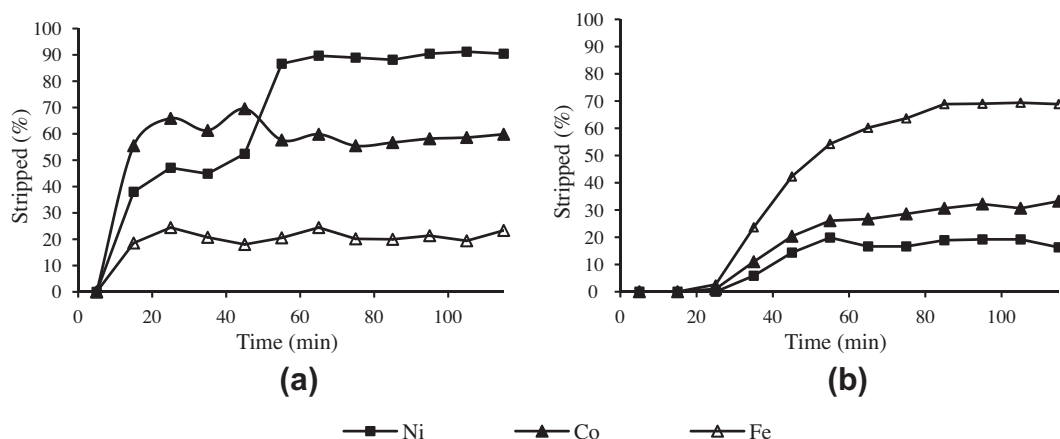
Fig. 16. Continuous test results for stripping of the organic phase with the higher metal loading (plant configuration in Fig. 12); (a) and (b) represent the 1st and 2nd stages, respectively.

The results for the test performed with the lower metal loading on the organic phase (0.94 g/l Ni, 0.37 g/l Co and 1.37 g/l Fe) are shown in Fig. 15. Although the nickel and cobalt extraction in the first stage remained approximately constant from 45 min onwards, the iron stripping continued to decrease gradually up to 85 min, at which point the test was completed; steady state conditions could also not be achieved in the second stripping stage. From 65 to 85 min the percentage of nickel and cobalt stripped in the first stage were approximately 98.7% and 76.0%, respectively, while 5.4–10.5% of the iron was also stripped. The batch test results predicted virtually complete stripping of both nickel and cobalt, with no stripping of iron. After the second stage stripping, cobalt removal was still incomplete with an overall stripping percentage of approximately 83.9%. The iron stripping of approximately 30% in the second stage was significantly lower than the 99.5% predicted by the batch test results. It is believed that the main reason for the low iron extraction was because the agitation time was too short for equilibrium to be reached. The mixer residence time of 3.7 min achieved with the mixer-settler setup is much shorter than the 10 min of agitation utilised for the batch tests. For this reason, the second stage stripping was expanded to include a second mixer in the subsequent test in order to increase the agitation time to allow higher iron stripping to be achieved.

The results for the test performed with the higher metal loading on the organic phase (3.07 g/l Ni, 0.96 g/l Co and 2.50 g/l Fe) are shown in Fig. 16. Steady state conditions in the first and second stripping stages were achieved after approximately 65 min and 85 min, respectively. The percentage nickel, cobalt and iron stripped in the first stage are approximately 89.3%, 58.3% and 21.7%, while a further 69.2% of the iron originally present on the organic phase is stripped during the second stage stripping. The higher nickel and cobalt loading of the organic hence resulted in 9.4% and 17.7% lower nickel and cobalt stripping in the first stage compared to nickel and cobalt stripping achieved for the organic with the lower metal loading, respectively. The increased agitation time and higher A/O ratio utilised in the second stripping stage did yield a significantly higher percentage iron stripping compared to the continuous test performed for the lower metal loading.

4. Conclusions

The O/A ratio and NaOH addition were found to be the two process parameters with the most significant effect on the nickel preloading, while the O/A ratio and nickel loading have the largest effect on cobalt and iron extraction. Virtually all the iron and 95–96% cobalt could be extracted from the nickel sulphate leach solution in a single batch test, while nickel extraction was insignificant. The sodium addition to the nickel sulphate product solution increased as the O/A ratio and nickel loading increased. This is due to the fact that higher nickel loadings require higher sodium additions in the preloading stage, which increases the probability of sodium uptake by the organic phase and consequently ends up in the purified nickel stream. The operating conditions proposed based on the batch test results achieved sufficient removal of iron and cobalt in continuous tests, and the performance proved to be insensitive to a 20% increase in the iron content of the feed solution.

The A/O ratio and acid concentration were found to be the two process parameters that have a significant effect on the stripping of Ni, Co, and Fe. Increasing the metal loading of the organic phase will require a higher A/O ratio and/or higher stripping agent concentration to be used. Selective stripping of nickel and cobalt are limited by phase separation problems and is therefore not practical. Based on the batch test results, separation of nickel and cobalt from iron using selective stripping is possible. These results could not be reproduced in continuous tests, but this is believed to be primarily as a result of an insufficiently short agitation time achieved with the mixer-settler setup.

Based on these results, it can be concluded that a process flow sheet utilising the Cyanex 272 preloading configuration can be used for the treatment of the crude nickel sulphate leach solution produced in the first leach stage of the modified Sherrit® process to remove dissolved cobalt and iron prior to $NiSO_4 \cdot 6H_2O$ production. It is proposed that the extraction stage be operated with a nickel loading between 2.95 g/l and 3.95 g/at an O/A ratio of 1.5. This nickel loading can be produced in a single preloading stage using a recycled portion of the nickel sulphate product stream as the aqueous phase. The stripping of the loaded organic phase should be performed in two stages with cobalt and nickel being stripped in the first stage using a 0.1 M H_2SO_4 solution at an A/O ratio of 3, followed by iron stripping in the second stage using 1 M H_2SO_4 solution at an A/O ratio of 0.75. Methods for treatment of the less acidic cobalt containing solution (for recovery of cobalt as a marketable product) and the more acidic iron containing waste stream (for minimisation of environmental impact) still need to be investigated.

References

Bhaskara Sarma, P., Reddy, B., 2002. Liquid-liquid extraction of nickel at macro-level concentration from sulphate/chloride solutions using phosphoric acid based extractants. Minerals Engineering 15 (6), 461–464.

Casas, J.M., Paipa, C., Godoy, I., Vargas, T., 2007. Solubility of sodium-jarosite and solution speciation in the system Fe(III)–Na–H_2SO_4–H_2O at 70C. Geochemical Exploration 92, 111–119.

Devi, N., Nathsarma, K., Chakravortty, V., 1998. Separation and recovery of cobalt (II) and nickel (II) from sulphate solutions using sodium salts of D2EHPA, PC 88A and Cyanex 272. Hydrometallurgy 49 (1–2), 47–61.

Devi, N., Nathsarma, K., Chakravortty, V., 1994. Sodium salts of D2EHPA, PC-88A and Cyanex-272 and their mixtures as extractants for cobalt (II). Hydrometallurgy 34 (3), 331–342.

Dorfling, C., Akdogan, G., Bradshaw, S.M., Eksteen, J.J., 2011. Determination of the relative leaching kinetics of Cu, Rh, Ru and Ir during the sulphuric acid pressure leaching of leach residue derived from Ni–Cu converter matte enriched in platinum group metals. Minerals Engineering 24 (6), 583–589.

Flett, D.S., 2005. Solvent extraction in hydrometallurgy: the role of organophosphorus extractants. Journal of Organometallic Chemistry 690 (10), 2426–2438.

Habashi, F., 1999. Textbook of Hydrometallurgy, second ed. Métallurgie Extractive Québec, Québec, Canada, p. 478.

Hubicki, Z., Hubicka, H., 1996. Studies on the extraction process of nickel (II) sulphate purification using Cyanex 272. Hydrometallurgy 40 (1–2), 65–76.

Ismael, M.R.C., Carvalho, J.M.R., 2003. Iron recovery from sulphate leach liquors in zinc hydrometallurgy. Minerals Engineering 16 (1), 31–39.

Nogueira, C.A., Oliveira, P.C., Pedrosa, F.M., 2009. Separation of cadmium, cobalt, and nickel by solvent extraction using the nickel salts of the extractants. Solvent Extraction and Ion Exchange 27 (2), 295–311.

O'Callaghan, J., Chamberlain, T., 2002. Solvent extraction of impurity metals from a valuable metal sulphate solution. European Patent EP1252345.

Olivier, M.C., Dorfling, C., Eksteen, J.J., 2011. Extraction of cobalt(II) and iron(II) from nickel(II) solutions with nickel salts of Cyanex 272. Proceedings of the 19th International Solvent Extraction Conference, 3–7 October 2011, Santiago, Chile.

Park, K.H., Mohapatra, D., 2006. Process for cobalt separation and recovery in the presence of nickel from sulphate solutions by Cyanex 272. Metals and Materials International 12 (5), 441–446.

Ritcey, G.M., 1980. Crud in solvent extraction processing – a review of causes and treatment. Hydrometallurgy 5 (2–3), 97–107.

Ritcey, G.M., 1986. Iron – an overview of its control in solvent extraction of metals. In: Dutrizac, J.E., Monhemius, A.J. (Eds.), Iron control in hydrometallurgy. Ellis Horwood Limited Publishers, Chichester, England, pp. 247–281.

Rodrigues, L.E.O.C., Mansur, M.B., 2009. Hydrometallurgical separation of rare earth elements, cobalt and nickel from spent nickel-metal-hydride batteries. Journal of Power Sources 195 (11), 3735–3741.

Thyse, E.L., Akdogan, G., Eksteen, J.J., 2011. The effect of changes in iron endpoint during Peirce Smith Converting on PGE containing nickel converter matte mineralisation. Minerals Engineering 24 (7), 688–697.

Van Schalkwyk, R.F., Eksteen, J.J., Petersen, J., Thyse, E.L., Akdogan, G., 2011. An experimental evaluation of the leaching kinetics of PGM-containing Ni–Cu–Fe–S Peirce Smith converter matte, under atmospheric leach conditions. Minerals Engineering 24 (6), 524–534.